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(B) Inventors (including city and state or foreign country of residence, for each)
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(C) Title: Ethoxylated Surfactants for Water in Oil Emulsions

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(H) 23 Pages of Specification 4 Pages of Claims
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(I) A duplicate of this Cover Sheet is attached.

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3237

TITLE: ETHOXYLATED SURFACTANTS FOR WATER IN OIL EMULSIONS

5 **Related Application**

This is a continuation in part of USSN 18/319668 filed on 12/13/02 entitled "An Emulsified Water Blended Fuels Produced By Using A Low Energy Process And Novel Surfactant."

Field of Invention

10 The invention relates to a novel additive package to produce a water in oil emulsion, in particular water blended fuels with good emulsion stability.

Background of the Invention

Internal combustion engines, especially diesel engines, using water fuel blends results in the combustion chamber producing lower nitrogen
15 oxides (NO_x), hydrocarbons and particulate matter emissions. NO_x emissions have become an important environmental issue because it contributes to smog and air pollution. Governmental regulations and environmental concerns have driven the need to reduce NO_x emissions from engines. In particular, the U.S. Clean Air Act will require about 90% to 95%
20 reduction of the current level of internal combustion engines emissions by the year 2007. Similar regulations are expected in Europe and other parts of the industrialized world.

Diesel fueled engines produce NO_x due to the relatively high flame temperatures reached during combustion. The reduction of NO_x production
25 conventionally includes the use of catalytic converters, using "clean" fuels, recirculation of exhaust and engine timing changes. These methods are typically expensive or complicated to be readily commercially available. Water is inert toward combustion, but lowers the peak combustion temperature resulting in reduced particulates and NO_x formation. When
30 water is added to the fuel it forms an emulsion and these emulsions are generally unstable. Stable water in fuel emulsions of a small particle size are difficult to reach and maintain.

An emulsion fuel has to meet the specifications of diesel fuel, as well as additional specifications which relate to an emulsion fuel. For instance the Italian National specification (Decreto 20 marzo 2000, published on 3rd April 2000 in Gazzetta Ufficiale, n.78) imposes a stability test criterion, defined by a centrifuge test (AFNOR prNFM 07-101). In the Italian specification a sample of emulsion (defined as containing 12-15% water by weight) is subjected to centrifugation (at a relative centrifugal force of 4200 for 5 minutes) and must show (i) no free water and, (ii) a sedimented layer of compressed water emulsion not exceeding 9% by volume. The standard also stipulates that no free water must be formed for a further period of 4 months. The French National specification defines similar criteria for emulsion stability.

Another important aspect of emulsion technology is the energy required in order to make the emulsions. Various technologies are available, for instance static mixers, rotor-stator mills and ultrasonic devices. Whichever technology is employed an important characteristic of a good emulsion system (i.e. the two immiscible phases, the surfactants and carrier fluids) is that it should emulsify quickly and, without undue high expenditure of energy, form the desired emulsion giving a good particle size distribution.

The use of emulsified fuels have been disclosed in other patents and patent applications of Applicant, such as USPN 6,280,485, 6,383,237, 6,368,367, 6,368,366 and 6,280,485 and USSN 09/761,482 all incorporated herein by reference and assigned to the assignee of the present application.

It would be advantageous to develop a stable water in fuel emulsion. Further, it would be advantageous to make more stable additive surfactant package for the use in water in oil emulsions.

The present invention has discovered the use of surfactants to make a water in oil emulsion/fuels. Further, the present invention has discovered that a fatty amine ethoxylate and derivatives of a PiB succinate surfactant is advantageous to produce a water-in oil emulsion because (1) emulsification occurs readily (low residence time in the mixer); (2) more stable emulsions are formed; (3) in addition to the excellent colloidal properties the resultant

emulsified fuels show a markedly improved performance in use with respects to elastomer compatibility and corrosion; and (4) significant improvement in the overall stability and ease of handling of the additive surfactant package.

The term "NO_x" is used herein to refer to any of the nitrogen oxides, NO, NO₂, N₂O, or mixtures of two or more thereof. The terms "water-in-oil" emulsion, "water emulsion", "emulsions", "water blended fuel", "emulsified water fuel" and other variations are interchangeable.

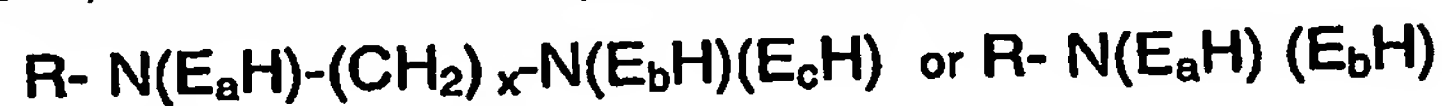
Summary of the Invention

The invention relates to an emulsified water in oil composition comprising:

- 10 a. a fuel in the range of about 50% to about 99% by weight of the composition;
- b. a water in the range of about 1% to about 50% by weight of the composition;
- c. a polyisobutenyl succinic anhydride (PIBSA) derived emulsifier
- 15 wherein the molecular weight of the PIB chain is in the range of about 200 to 5000 and in the range of about 0.01 % to about 10%, or more preferred 0.02% to 5%, or more preferred 0.03% to 1.5%, by weight of the composition;
- d. an alkylamine ethoxylated surfactant in the range of about 0.01% to about 10%, or more preferred 0.02% to 5%, or more preferred 0.03% to 1.5%, by weight of the composition; and
- 20 e. optionally at least one of a functional amount of at least one water-soluble, oil-soluble functional additive dissolved in the emulsified aqueous phase such as ammonium nitrate.

25 In particular the surfactant comprises:

(a) at least one of an alkylamine ethoxylated surfactant that can be a mono- or a di- amine of the general formulae:



wherein R equals straight or branched chained alkyl group, C8 to C30, or more preferred C10 to C24, and saturated or unsaturated, containing either 0, or 1, or 2 or 3 double bonds;

N = nitrogen atom;

E is an ethoxylate group, $-\text{CH}_2-\text{CH}_2-\text{O}-$

x is either 1, 2, or 3, and

a, b, c, is an integer from 0 to 20 such that: $a+b+c =$ any value between 1 and 20, more preferably between 1 and 14; and

5 (b) at least one PIBSA-derived material (with a PIB chain in the molecular weight in the range of 200 to 5000) comprising:

(1) a PIBSA itself;

(2) a PIB succinic acid, wherein this material can be prepared by reacting a PIBSA with water;

10 (3) a PIB succinic acid - amine salt wherein this material can be prepared by reacting the PIB succinic acid as described in (2) with either an alkyl amine (primary, secondary, or tertiary) or an ethanolamine and/or ethoxylated amine (A) described above and wherein this salt can be a fully neutralised or partially neutralised salt;

15 (4) a PIB succinic aminoalkylester or ester-acid or amine salt thereof. This material can be prepared by reacting the PIBSA or PIB succinic acid as described in (1) and (2) or ester thereof with a hydroxylamine or an alkanol amine like ethanolamine and/or ethoxylated amine (A) described above, wherein the salt can be a fully neutralised or
20 partially neutralised salt;

(5) a succinimide or succinamide or amide-acid salt thereof derived by reacting PIBSA with an amine or poly amine;

(6) a succinic ester derived by reacting PIBSA with a polyol; or

(7) combinations thereof.

25 Further, the invention relates to a process for making a water in oil emulsion comprising emulsifying a fuel, a water, a PIBSA-derived surfactant, and an alkylamine ethoxylated surfactant. The invention further relates to a process to produce an emulsified water in oil composition from a concentrate comprising emulsifying a portion of a fuel, a portion to
30 substantially all of a water, substantially all of the PIBSA-derived surfactant, substantially all of the alkylamine ethoxylated surfactant to form a concentrate emulsion; and then diluting the concentrated emulsion with the

remaining portion of fuel at the time of use.

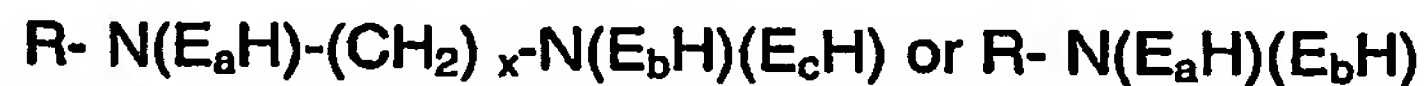
The water in oil emulsion provides good emulsion stability. The additive package allows for the water in oil emulsion to be processed more easily. Further the emulsion has increased storage stability. The water in oil composition is useful as a fuel for stationary and/or combustion engines and/or open flame burning apparatus.

Detailed Description

The invention discloses an additive surfactant package of at least two surfactants to produce a stable emulsified water in oil composition. The emulsified water in oil composition employs a PIBSA derived surfactant and an alkylamine ethoxylated surfactant which are identified by the term additive surfactant package herein. The additive surfactant package has properties to lower the interfacial tension at the water/oil interface during emulsion formation.

The additive surfactant package is in the range of about 0.001% to about 15%, in another embodiment about 0.01% to about 10%, in another embodiment about 0.05% to about 5%, and in another embodiment about 0.1% to about 3% by weight of the water in oil composition. The additive surfactant package maybe used in combination with other surfactants which may be either ionic or non-ionic surfactant.

The alkylamine ethoxylated surfactant may be derived from a mono- or a di-amine and has the general formulae:



wherein R =, straight or branched chained alkyl group, C8 to C30, preferably between C10 and C24, more preferably C12 to C22 and most preferable C14 to C20 and saturated or unsaturated, contained either 0, or 1, or 2 or 3 double bonds;

N = nitrogen atom;

E is an ethoxylate group, $-CH_2-CH_2-O-$;

x = 1, 2, or 3; and

a, b, c, = any integer between 0 and 20 such that: $a+b+c$ = any value between 1 and 20, more preferably between 1 and 14.

In another embodiment R is about C12 to about C22, and in another embodiment about C10 to about C20.

The PIBSA-derived derived surfactant is selected from at least one of or combinations of:

- 5 (1) a PIBSA itself.
- (2) a PIB succinic acid. This material can be prepared by reacting a PIBSA with water.
- (3) A PIB succinic acid - amine salt. This material can be prepared by reacting the PIB succinic acid as described in (2) with either an
10 alkyl amine (primary, secondary, or tertiary), or an ethanolamine and/or ethoxylated amine (A) described above. This salt can be a fully neutralised or partially neutralised salt.
- (4) A PIB succinic aminoalkylester or ester-acid or amine salt thereof. This material can be prepared by reacting the PIBSA or PIB
15 succinic acid as described in (1) and (2) or ester thereof with a hydroxylamine or an alcohol amine like ethanolamine and/or ethoxylated amine (A) described above, wherein the salt can be a fully neutralised or partially neutralised salt.
- (5) A succinimide or succinamide or amide-acid salt thereof
20 derived by reacting PIBSA with an amine or poly amine.
- (6) A succinic ester derived by reacting PIBSA with a polyol.

The PIB based surfactant includes both non-ionic, ionic materials or combinations thereof. The non-ionic materials include PIB succinic acid and PIB succinamides. The ionic materials include PIB succinic acid salts.
25 These are prepared by reaction of the succinic acid with diethylethanolamine. Another embodiment of the ionic material is an amidic acid salt.

The polyisobutylene chain of the PIBSA-derived surfactant has a number average molecular weight of about 200 to about 5000, in one
30 embodiment about 1800 to about 2300, in one embodiment about 300 to about 3000, in one embodiment about 700 to about 1300, in one embodiment about 800 to about 1000, and in one embodiment from 300 to

600. The PIBSA from which the PIBSA-derived surfactant is prepared is characterized by about 1.3 to about 2.5, and in one embodiment about 1.7 to about 2.1, succinic groups per equivalent weight of the polyisobutylene substituent. In one embodiment, the hydrocarbyl-substituted carboxylic acid acylating agent is a polyisobutene-substituted succinic anhydride, the
5 polyisobutene substituent having a number average molecular weight of about 1,500 to about 3,000, and in one embodiment about 1,800 to about 2,300, said first polyisobutene-substituted succinic anhydride being characterized by about 1.3 to about 2.5, and in one embodiment about 1.7 to
10 about 2.1, in one embodiment about 1.0 to about 1.3, and in one embodiment about 1.0 to about 1.2 succinic groups per equivalent weight of the polyisobutene substituent.

Examples of alkylamines disclosed in (2) above include but are not limited to ethylamine, diethylamine, n-butylamine, di-n-butylamine,
15 allylamine, isobutylamine, cocoamine, stearylamine, laurylamine, methyllaurylamine, oleylamine, N-methyloctylamine, dodecylamine, and octadecylamine. Suitable examples of tertiary monoamines include but are not limited to trimethylamine, triethylamine, tripropylamine, tributylamine, monoethyldimethylamine, dimethylpropylamine, dimethylbutylamine,
20 dimethylpentylamine, dimethylhexylamine, dimethylheptylamine, and dimethyloctylamine.

The amines include but are not limited to hydroxyamines, such as mono-, di-, and triethanolamine, dimethylethanol amine, diethylethanol amine, di-(3-hydroxy propyl) amine, N-(3-hydroxybutyl) amine, N-(4-hydroxy
25 butyl) amine, and N,N-di-(2-hydroxypropyl) amine; alkylene polyamines such as methylene polyamines, ethylene polyamines, butylene polyamines, propylene polyamines, pentylene polyamines, and the like. Specific examples of such polyamines include but are not limited to ethylene diamine, diethylene triamine, triethylene tetramine, propylene diamine, trimethylene
30 diamine, tripropylene tetramine, tetraethylene pentamine, hexaethylene heptamine, pentaethylene hexamine, or a mixture of two or more thereof;

ethylene polyamine bottoms or a heavy polyamine. In a preferred embodiment the alkanolamine is diethyl ethanolamine.

The PIBSA-derived emulsifier may be present in the water fuel emulsion at a concentration of 0.01% to about 10% by weight based on the overall weight of the emulsion, and in one embodiment about 0.02 to about 5% by weight, and in one embodiment about 0.03 to about 1.5% by weight.

Examples of suitable alkylamine ethoxylated surfactants include but are not limited to tallow amine penta ethoxylate, tallow amine tetra ethoxylate, tallow amine hexa ethoxylate, tallow amine hepta ethoxylate, oleyl amine deca ethoxylate, oleyl amine undeca ethoxylate, oleyl amine nona ethoxylate, oleyl amine dodeca ethoxylate, tris(2-hydroxyethyl)-N-tallowalkyl-1,3-diaminopropane, oleyl amine penta ethoxylate, oleyl amine diethoxylate, stearyl alcohol penta ethoxylate and stearyl amine diethoxylate. In one embodiment the alkylamine ethoxylated surfactant is tallow amine penta ethoxylate. In one embodiment the alkylamine ethoxylated surfactant is oleyl amine deca ethoxylate. In one embodiment the alkylamine ethoxylated surfactant is tris(2-hydroxyethyl)-N-tallowalkyl-1, 3-diaminopropane. The alkylamine ethoxylated surfactant can be used alone or in combination.

The ethoxylated amine surfactant may be present in the water fuel emulsion at a concentration of 0.01% to about 10% by weight based on the overall weight of the emulsion, and in one embodiment about 0.02 to about 5% by weight, and in one embodiment about 0.03 to about 1.5% by weight.

Further other surfactants may be used in combination with the additive surfactant package but do not take the place of the additive surfactant package and include but are not limited to a) natural fats; b) ionics excluding the additive surfactant package c) co-surfactants; d) fatty acids and their amine salts; e) ethoxylate alcohols and f) combinations thereof.

The other non ionic and ionic surfactants include but are not limited to alkyl ethoxylates, ethoxylated alkylphenols, alkyl glucosides, ethoxylated alcohols, ethoxylated amines, amides derived from fatty acids and/or alcohols, ethers or fatty alcohols, esters of fatty acids and the like. In

addition the non-ionic and ionic surfactants have a hydrophilic lipophilic balance (HLB) in the range of about 2 to about 40, in one embodiment, about 2 to about 10, in one embodiment about 10 to about 15 and in another embodiment about 4 to about 8. Examples of these non-ionic and ionic
 5 surfactants are disclosed in *McCutcheon's Emulsifiers and Detergents*, 1993, North American & International Edition. Preferably the non ionic surfactants are Neodol 25-3, C12 – C 14 alcohol with two ethoxylates and Ethomeen C12. The non ionic and ionic surfactants may be used alone or in combination.

10 The natural fat surfactants include but are not limited to triglycerides, hydrolyzed triglycerides, oxidized products of triglycerides, vegetable oils, refined vegetable oils, used vegetable oils and the like. The preferred natural fat surfactant is a refined used vegetable oil. The natural fats can be used alone or in combination.

15 The co-surfactant has sufficient polar groups to render the co-surfactant partially soluble in both phases. The co-surfactants include but are not limited to alcohols, amines, amides, esters, ketones, ethers and mixtures thereof. The co-surfactant has at least 1 to about 24, in another embodiment about 1 to about 10, in another embodiment about 1 to about 8
 20 carbon atoms. The co-surfactants may be used alone or in combination.

The fatty acids and their amine salts include but are not limited to N,N-diethyl ethanolamine salts of oleic acid, tall oil fatty acids, stearic acid, palmitic acid, lauric acid and the like. The preferable fatty acid and their amine salt is oleic acid–diethyl ethanol amine salt. The fatty acids and their
 25 amine salts can be used alone or in combination.

Fuel

The fuel comprises hydrocarbonaceous petroleum distillate fuel, non-hydrocarbonaceous materials that include but are not limited to water, oils, liquid fuels derived from vegetable sources, liquid fuels derived from
 30 minerals, liquid to gas, and mixtures thereof. Suitable fuels include, but are not limited to, gasoline, diesel, kerosene, naphtha, aliphatics and paraffin. The fuel comprises non-hydrocarbonaceous materials include but is not

limited to alcohols such as methanol, ethanol and the like, ethers such as diethyl ether, methyl ethyl ether and the like, organo-nitro compounds and the like; fuels derived from vegetable or mineral sources such as corn, alfalfa, shale, coal and the like. The fuel also includes but is not limited to
5 gas to liquid fuels, Fischer-Tropsch fuels and the like. The fuel also includes but is not limited to mixtures of one or more hydrocarbonaceous fuels and one or more non-hydrocarbonaceous materials. Examples of such mixtures are combinations of gasoline and ethanol and of diesel fuel and ether and the like.

10 In one embodiment, the fuel is any gasoline. Including, but not limited to a chlorine-free gasoline or a low-chlorine gasoline, or a low sulfur gasoline or sulfur-free gasoline and the like.

In one embodiment, the fuel is any diesel fuel. The diesel fuels include, but are not limited to, those that contain alcohols and esters, has a
15 sulfur content of up to about 0.05% by weight or sulfur-free, is a chlorine-free or low-chlorine diesel fuel and the like. In one embodiment the preferred fuel is a diesel fuel.

The fuel is present in the emulsified fuel at a concentration of about 50% to about 95% by weight, and in one embodiment about 60% to about
20 95% by weight, and in one embodiment about 65% to about 85% by weight, and in one embodiment about 80% to about 90% by weight of the emulsified fuel.

Water

The water used in the emulsified fuel may be taken from any source.
25 The water includes but is not limited to tap, deionized, de-ionized to a conductivity of <30 microsiemens/cm and up to 50% v/v, demineralized, purified, for example, using reverse osmosis or distillation, and the like. The water includes water mixtures that further includes but are not limited to antifreeze components such as alcohols and glycols, ammonium salts such
30 as ammonium nitrate, ammonium maleate, ammonium acetate and the like, and combinations thereof; and other water soluble additives.

The water is present in the emulsified fuel at a concentration of about 1% to about 50% by weight, in one embodiment about 5% to about 40% being weight, in one embodiment about 5% to about 25% by weight, and in one embodiment about 10% to about 20% by weight of the emulsified fuel.

- 5 In another embodiment the water is present in the emulsified fuel at a concentration of less than 1% by weight, in another embodiment less than 0.5% by weight, in another embodiment less than 0.1% by weight, and in another embodiment in the range of about 0.1% to about 1% by weight of the emulsified fuel; An emulsified water in oil composition can be made with
10 water at these low levels with the fuel, the emulsifier, the surfactant and optionally ammonium nitrate and in another embodiment without the surfactant and with the fuel, the emulsifier and optionally the ammonium nitrate.

Other Additives

- 15 In one embodiment, the emulsified fuel contains a cetane improver. The cetane improvers that are useful include but are not limited to peroxides, nitrates, nitrites, nitrocarbmates and the like. Useful cetane improvers include but are not limited to nitropropane, dinitropropane, tetranitromethane, 2-nitro-2-methyl-1-butanol, 2-methyl-2-nitro-1-propanol,
20 and the like. Also included are nitrate esters of substituted or unsubstituted aliphatic or cycloaliphatic alcohols which may be monohydric or polyhydric. These include substituted and unsubstituted alkyl or cycloalkyl nitrates having up to about 10 carbon atoms, and in one embodiment about 2 to about 10 carbon atoms. The alkyl group may be either linear or branched, or
25 a mixture of linear or branched alkyl groups. Examples include but are not limited to methyl nitrate, ethyl nitrate, n-propyl nitrate, isopropyl nitrate, allyl nitrate, n-butyl nitrate, isobutyl nitrate, sec-butyl nitrate, isooctyl nitrate, tert-butyl nitrate, n-amyl nitrate, isoamyl nitrate, 2-amyl nitrate, 3-amyl nitrate, tert-amyl nitrate, n-hexyl nitrate, n-heptyl nitrate, n-octyl nitrate, 2-ethylhexyl
30 nitrate, sec-octyl nitrate, n-nonyl nitrate, n-decyl nitrate, cyclopentyl nitrate, cyclohexyl nitrate, methylcyclohexyl nitrate, and isopropylcyclohexyl nitrate. Also useful are the nitrate esters of alkoxy-substituted aliphatic alcohols such

as 2-ethoxyethyl nitrate, 2-(2-ethoxy-ethoxy) ethyl nitrate, 1-methoxypropyl-2-nitrate, 4-ethoxybutyl nitrate, etc., as well as diol nitrates such as 1,6-hexamethylene dinitrate. A useful cetane improver is 2-ethylhexyl nitrate.

5 The concentration of the cetane improver in the emulsified fuel is at any concentration sufficient to provide the emulsion with the desired cetane number. In one embodiment, the concentration of the cetane improver is at a level of up to about 10% by weight, and in one embodiment about 0.05% to about 10% by weight, and in one embodiment about 0.05% to about 5% by weight, and in one embodiment about 0.05% to about 1% by weight of
10 the emulsified fuel.

In addition to the foregoing materials, other fuel additives that are known to those skilled in the art may be used in the emulsified fuel. These include but are not limited to dyes, rust inhibitors such as alkylated succinic acids and anhydrides, bacteriostatic agents, gum inhibitors, metal
15 deactivators, upper cylinder lubricants and the like.

The additives, including the foregoing emulsifiers, may be diluted with a substantially inert, normally liquid organic solvent such as naphtha, benzene, toluene, xylene or diesel fuel to form an additive concentrate which is then mixed with the fuel and water to form the emulsified fuel.

20 The emulsified fuel may contain up to about 60% by weight organic solvent, and in one embodiment about 0.01% to about 50% by weight, and in one embodiment about 0.01% to about 20% by weight, and in one embodiment about 0.1% to about 5% by weight, and in one embodiment about 0.1% to about 3% by weight of the emulsified fuel.

25 The emulsified fuel may additionally contain an antifreeze agent. The antifreeze agent is typically an alcohol. Examples include but are not limited to ethylene glycol, propylene glycol, methanol, ethanol, glycerol and mixtures of two or more thereof. The antifreeze agent is typically used at a concentration sufficient to prevent freezing of the water used in the water
30 fuel emulsion. The concentration is therefore dependent upon the temperature at which the fuel is stored or used. In one embodiment, the concentration is at a level of up to about 20% by weight of the emulsified

fuel, and in one embodiment about 0.1% to about 20% by weight, and in one embodiment about 1% to about 10% by weight of the emulsified fuel.

5 The total concentration of the additives, in the emulsified fuel is from about 0.05% to about 30% by weight, and in one embodiment about 0.1% to about 20% by weight, and in one embodiment about 0.1% to about 15% by weight, and in one embodiment about 0.1% to about 10% by weight, and in one embodiment about 0.1% to about 5% by weight of the emulsified fuel.

Process

10 The water in oil emulsion is comprised of a continuous fuel-phase, a discontinuous water or aqueous phase, an emulsifying amount of an additive surfactant package and optionally other a surfactants and optionally a functional additives such as ammonium nitrate.

15 In the practice of the present invention the water in oil emulsion is made by a batch, semi-batch or a continuous process. A concentrate may be made and used. The process is capable of monitoring and adjusting the flow rates of the fuel, additive, surfactant, package, surfactants, other additives and/or water to form a stable emulsion with the desired water droplet size. The water phase of the emulsified fuel is comprised of droplets having a mean diameter of about 1.0 microns or less, in another
20 embodiment about 0.8 microns or less, in another embodiment about 0.5 microns or less, in another embodiment about 0.15 microns or more, in another embodiment about 1.0 micron to about 0.5 microns, and in another embodiment about 1.0 micron to about 0.2 microns.

25 The emulsified fuel may be prepared by the steps of mixing the fuel, the emulsifier, the additive surfactant package, and other oil soluble additive using shear techniques to form the fuel additive mixture. Then the fuel additive mixture is mixed with water and optionally any desired water soluble additives to form the desired emulsified water blended fuel.

30 In a batch process the water, the additive surfactant package, the fuel and optional additives are added to a tank, in the desired amounts, The mixture is emulsified using an emulsification device in the vessel, or alternatively the mixture flows from the vessel via a circular line to the

emulsification device which is external to the vessel, for about 1 to about 20 tank turnovers. The temperature in the range of about ambient temperature to about 100°C (212°F), and in another embodiment in the range of about 4°C (40°F) to about 65°C (150°F), and at a pressure in the range of about
5 atmospheric pressure to about 10 atmospheres, in another embodiment about atmospheric pressure to about 80 psi, in another embodiment in the range of about 1 to about 2 atm (15 psi to about 30 psi).

The continuous process described herein depicts another embodiment of the invention. The feeds of the fuel, additive surfactant
10 package, water and optional additives are introduced as discrete feeds or in the alternative combinations of the discrete feeds. The processing streams are introduced in or as close to the inlet of the emulsification device as possible. It is preferable that the emulsifier is added to the fuel as a fuel emulsifier stream prior to the discrete feeds combining together. The
15 continuous process generally occurs under ambient conditions. The continuous process is generally done at atmospheric pressure to about 35 atm (500 psi), in another embodiment in the range of about atmospheric pressure to about 8 to 9 atm (about 120 psi), and in another embodiment in the range of about atmospheric pressure to about 4 atm (about 50 psi). The
20 continuous process generally occurs at ambient temperature. In one embodiment the temperature is in the range of about ambient temperature to about 100 °C (212°F), and in another embodiment in the range of about 4°C (40°F) to about 65°C (150°F).

Alternatively, a concentrate is formed and all or substantially all the
25 water, and water soluble additive and a portion of the fuel and all or substantially all the surfactant packages is emulsified under shear conditions to form a concentrate fuel. The emulsified fuel, when used, is then blended under normal mixing conditions with the remaining portion remaining portion of the fuel.

30 The process may be in the form of a containerized equipment unit that operates automatically. The process can be programmed and monitored locally at the site of its installation, or it can be programmed and monitored

from a location remote from the site of its installation. The fully formulated water fuel blend is optionally dispensed to end users at the installation site, or in another embodiment end users can blend the concentrated emulsion with the final portion of fuel. This provides a way to make the water in fuel emulsions available to end users in wide distribution networks.

The emulsification may occur at shear conditions are greater than $50,000 \text{ s}^{-1}$. However, the composition may be emulsified at shear process conditions and occurs at a shear rate in the range of less than or equal to $50,000 \text{ s}^{-1}$; and in another embodiment less than about $20,000 \text{ s}^{-1}$, and in another embodiment less than about $1,000 \text{ s}^{-1}$, and in another embodiment less than 100 s^{-1} , and in another embodiment less than 1 s^{-1} . If more than one emulsification step is used, the shear rates of the emulsification steps can be the same, similar or different, depending on the emulsifier and low molecular weight surfactant used. The emulsification provides for the desired particle size and a uniform dispersion of water in the fuel.

The emulsification occurs by any shear method used in the industry including but not limited to mixing, mechanical mixer agitation, static mixers, centrifugal pumps, positive displacement pumps, orifice plates, and the like. Examples of the devices include but are not limited to an Aquashear, pipeline static mixers, rotor/stator mixers and the like. The Aquashear is a low-pressure hydraulic shear device. The Aquashear mixers are available from Flow Process Technologies Inc.

Engines

The engines that may be operated in accordance with the invention include all (internal combustion) engines including spark ignited (gasoline) and compression ignited (diesel) for both mobile including locomotive, marine, automotive, truck, heavy duty, aviation and the like, and stationary power plants. The engines may be two-cycle or four-cycle. The engines may employ conventional after treatment devices. Included are on- and off-highway engines, including new engines as well as in-use engines.

An open-flame burning apparatus may be operated with the emulsified water fuel blend of the invention. The open-flame burning

apparatus may be any open-flame burning apparatus equipped to burn a liquid fuel. These include domestic, commercial and industrial burners. The industrial burners include those requiring preheating for proper handling and atomization of the fuel. Also included are oil fired combustion units, oil fired power plants, fired heaters and boilers, and boilers for use in ships including deep draft vessels. The fuel burning apparatus may be a boiler for commercial applications included are boilers for power plants, utility plants, and large stationary and marine engines. The open-flame fuel burning apparatus may be an incinerator or a rotary kiln incinerator, liquid injection kiln, fluidized bed kiln, cement kiln, and the like. Also included are steel and aluminium forging furnaces. The open-flame burning apparatus may be equipped with a flue gas recirculation system.

Specific Embodiments

Example 1

A fuel emulsion is prepared by mixing about 13g of de-ionised water, about 84.5g of a commercially available diesel containing less than 50ppm of sulphur, about 0.523g of 2300 MW polyisobutylene succinic acid, about 0.06g of diethyl ethanolamine, about 0.562g of tallow amine 7 mole ethoxylate, about 0.305g of 2-ethylhexylnitrate and about 1g of diluent oil. The mixture is sheared by mixing in an Ultra Turrax T25B rotor-stator mixer for about 3 minutes.

Example 2

The emulsion is the same as Example 1 except the emulsion additionally contains about 0.12g of aqueous ammonium nitrate with about 54 % actives in solution.

Example 3

The emulsion is the same as Example 1 except the amounts of the following components in the emulsion are different, about 0.293g of 2300 MW polyisobutylene succinic acid, about 0.034g of diethyl ethanolamine and about 0.943g of tallow amine 7 mole ethoxylate and about 0.04g of

ammonium nitrate is added and the emulsion is sheared for about 30 seconds.

Example 4

5 The emulsion is the same as Example 3 except the emulsion is sheared for about 2 minutes.

Example 5

The emulsion is the same as Example 3 except the emulsion is sheared for about 5 minutes.

Example 6

10 The emulsion is the same as Example 1 except the amounts of the following components in the emulsion are different, about 0.375g of 2300 MW polyisobutylene succinic acid, about 0.043g of diethyl ethanolamine and about 0.807g of tallow amine 5 mole ethoxylate and about 0.04g of ammonium nitrate is added and the emulsion is sheared for about 30
15 seconds.

Example 7

The emulsion is the same as Example 6 except the emulsion is sheared for about 5 minutes.

Example 8

20 The emulsion is the same as Example 1 except the amounts of the following components in the emulsion are different, about 0.404g of 2300 MW polyisobutylene succinimide derived by reacting PIBSA with a polyamine and about 0.807g of tallow amine 5 mole ethoxylate and about 0.04g of ammonium nitrate is added and the emulsion is sheared for about 3 minutes.

25 Example 9

The emulsion is the same as Example 1 except the amounts of the following components in the emulsion are different, about 0.753g of 1000 MW

polyisobutylene succinimide derived by reacting PIBSA with a polyamine and about 0.35g of tallow amine 5 mole ethoxylate.

Example 10

- 5 The emulsion is the same as Example 1 except the amounts of the following components in the emulsion are different, about 0.258g of 1000 MW polyisobutylene succinic acid, about 0.142g of 550 MW polyisobutylene succinic acid, about 0.058g of diethyl ethanolamine, about 0.12g of ammonium nitrate and about 0.561g of tallow amine 7 mole ethoxylate.

Example 11

- 10 The emulsion is the same as Example 1 except the amounts of the following components in the emulsion are different, about 0.798g of 2300 MW polyisobutylene succinic acid, about 0.024g of diethyl ethanolamine, about 0.12g of ammonium nitrate, about 0.501g of tallow amine 7 ethoxylate and about 0.056g of oleyl amine 10 mole ethoxylate.

15 Test 1: Centrifuge Test

- Approximately 40g of emulsion is placed in calibrated, graduated conical centrifuge tube and placed in a swing-out rotor type centrifuge. The sample is centrifuged with a relative centrifugal force of about 4200 for about 5 minutes (as stipulated by the test method, AFNOR prNFM 07-101). The
20 stability of the emulsion is determined by measuring how much, if any, free water is produced and the amount of sediment formed. The minimum requirements are no free water and less than 9 volume % of the emulsion is sedimented out. The results obtained were Table I:

Table I

Example	Sediment volume %	Example	Sediment volume %
1	3.75	7	2.5
2	1.25	8	7.5
3	3.75	9	8.75
4	2.5	10	2.5
5	2.5	11	2.5
6	6.25		

Examples 1-11 produce no free water after 5 minutes. Overall Examples 1-11 pass the centrifuge test because they produce no free water and the amount of sediment formed is below 9 volume %. The test demonstrated that stable emulsions are produced.

Test 2: Particle Size

The particle size of an emulsion approximately 24 hours old is determined by placing about 600ml of diesel and about 0.5ml of emulsion in a Coulter LS230. The sample is exposed to a red laser and the diffraction of micelles and measured on a detector. The particle size distribution is then calculated. The results obtained are shown in Table II.

A laser light scattering instrument is used to measure the size distribution of water particles in PuriNOX™. When light encounters a particle, the particle scatters the light. The angular dependence of this scattered light is dependent on the size of the particle (relative to the wavelength of the incident light). By measuring the intensity of the scattered light as a function of angle, and by applying the Mie and Fraunhofer scattering theory, the particle size distribution can be determined. The Coulter LS230 uses an array of detectors to measure the intensity at 232 angles simultaneously.

Particle size of the emulsion was determined by laser light scattering technique (Coulter LS230 instrument) between 0.04 and >50 micron metres.

Table II

Example	% sub micron	Example	% sub micron
1	92.5	7	96.9
2	100	8	61.5
3	91.4	9	72.2
4	98	10	13.3
5	95.3	11	100
6	70.4		

- 5 Generally these measurements illustrate that excellent, substantially sub-micron emulsions are obtained in all case, with the exception of example 10. These data, in combination with the centrifuge data, point to formulations which are close to optimal and those (such as example 10) which are capable of improvement by alteration of the surfactants (e.g. by either changing the chemistry or changing the ratio of the surfactants).

10 Example 12 Formation of a novel ester/acid surfactants made by reacting PIB succinic anhydride (PIBSA) with fatty amine ethoxylates.

1. Synthesis:

- 15 Composition A: a PIBSA, (2300 m.w. Glissopal succinic anhydride), containing up to 30% solvent, was heated to about 80°C and held at this temperature while an equimolar quantity of tallow amine 7 mole ethoxylate was added over about 15 to about 30 minutes. The reaction was followed by IR until the anhydride peaks disappeared and the ester and carboxylic acid peaks appeared, indicating that a reaction was complete.

- 20 Composition B: A second preparation was carried out identical to Example A above except that the PIBSA was a 350 m.w. PIBSA.

Glissopal was obtained from BASF and 350 m.w. PIB was obtained from TCP.

2. Evaluation

Example 12: A fuel emulsion is prepared by mixing about 13g of de-ionised water, about 84.48g of a commercially available diesel containing less than 50ppm of sulphur, about 1.426g of the acid/ester illustrated in composition A above (i.e. made from 2300 MW polyisobutylene succinate and tallow amine 7 mole EO), about 0.305g of 2-ethylhexylnitrate, about 0.12g of aqueous (54% concentrate) ammonium nitrate and about 0.67g of diluent oil. The mixture is sheared by mixing in an Ultra Turrax T25B rotor-stator mixer for about 3 minutes.

Example 13: The emulsion is the same as Example 12 except the emulsion was made with 1.426g of the acid ester illustrated in Composition B above (i.e. made from 350 MW polyisobutylene succinate and tallow amine 7 mole EO).

Test 1: Centrifuge Test

Approximately 40g of emulsion is placed in calibrated, graduated conical centrifuge tube and placed in a swing-out rotor type centrifuge. The sample is centrifuged with a relative centrifugal force of about 4200 for about 5 minutes (as stipulated by the test method, AFNOR prNFM 07-101). The stability of the emulsion is determined by measuring how much, if any, free water is produced and the amount of sediment formed. The minimum requirements are no free water and less than 9 volume % of the emulsion is sedimented out. The results obtained are shown in Table III below.

25

Table III

Example	Sediment volume %	Example	Sediment volume %
12	6.25	13	2.5

Examples 12 and 13 produce no free water after 5 minutes. Overall Examples 12 and 13 pass the centrifuge test because they produce no free

water and the amount of sediment formed is below 9 volume %. The test demonstrated that stable emulsions are produced.

Test 2: Particle Size

The particle size of an emulsion approximately 24 hours old is determined by placing about 600 ml of diesel and about 0.5ml of emulsion in a Coulter LS230. The sample is exposed to a red laser and the diffraction of micelles and measured on a detector. The particle size distribution is then calculated. The results obtained are shown in Table IV below.

A laser light scattering instrument is used to measure the size distribution of water particles in PuriNOX™. When light encounters a particle, the particle scatters the light. The angular dependence of this scattered light is dependent on the size of the particle (relative to the wavelength of the incident light). By measuring the intensity of the scattered light as a function of angle, and by applying the Mie and Fraunhofer scattering theory, the particle size distribution can be determined. The Coulter LS230 uses an array of detectors to measure the intensity at 232 angles simultaneously.

Particle size of the emulsion was determined by laser light scattering technique (Coulter LS230 instrument) between 0.04 and >50 micron metres.

20

Table IV

Example	% sub micron	Example	% sub micron
12	81	13	100

Generally these measurements illustrate that excellent, substantially sub-micron emulsions are obtained in both case. These data, in combination with the centrifuge data, point to formulations which are close to optimal.

25

From the above description and examples the invention those skilled in the art may perceive improvements, changes and modifications in the

invention. Such improvement changes and modifications are intended to be covered by the appended claims.

What is Claimed:

1. An emulsified water in oil composition comprising:

- a) a fuel;
 - b) a water;
 - 5 c) an additive surfactants package comprising
 - i) an alkylamine ethoxylate, and
 - ii) a PIBSA-derived surfactant; and
 - d) optionally at least one of a functional amount of at least one
- water-soluble; oil-insoluble functional additive dissolved in the
- 10 emulsified aqueous phase.

2. The composition of claim 1 wherein the additive surfactant package comprises:

(a) at least one of an alkylamine ethoxylated surfactant that is a mono- or a di- amine of the general formulae and combinations thereof:

15 $R-N(E_aH)-(CH_2)_x-N(E_bH)(E_cH)$ or $R-N(E_aH)(E_bH)$

wherein R =, straight or branched chained alkyl group, C8 to C30, and saturated or unsaturated, containing either 0, or 1, or 2 or 3 double bonds, wherein N = nitrogen atom,

wherein E is an ethoxylate group, $-CH_2-CH_2-O-$,

20 wherein x = 1, 2, or 3, and

wherein a, b, c, = an integer from 0 to 20 such that $a+b+c$ = any value between 1 and 20; and

(b) at least one of a PIB based material comprising:

- (1) a PIBSA only;
- 25 (2) a PIB succinic acid;
- (3) a PIB succinic acid - amine salt;
- (4) a PIB succinic aminoalkylester or ester-acid or amine salt thereof;
- (5) a succinimide or succinamide or amide-acid salt thereof
- 30 derived by reacting PIBSA with an amine or poly amine;
- (6) a succinic ester derived by reacting PIBSA with a polyol;

or

(7) combinations thereof.

3. The composition of claim 2 wherein R is C10 to C24 and $a+b+c = 1$ to 14.
4. The composition of claim 2 wherein R is C12 to C22.
- 5 5. The composition on claim 1 wherein a fuel is in the range of about 50% to about 99% by weight of the composition; the water is in the range of about 1% to about 50% by weight of the composition; and the additive surfactant package is in the range of about 0.01% to about 10% by weight of the composition.
- 10 6. The composition of claim 1 wherein the water in oil composition is an emulsified water blended fuel and wherein the fuel is selected from the group comprising petroleum distillate fuel such as diesel, gasoline, fuel oil a mixture thereof; a fuel derived from vegetables, corn, alfalfa, rapeseed, soybeans, shale, coal or mixtures thereof; a biodegradable fuel; biodiesel;
- 15 residual fuel; bitumen; alcohol; ether; ethanol; Fischer-Tropsch fuels; gas to liquids fuels and combinations thereof.
7. The composition on claim 1 wherein the PIBSA-derived surfactant has a PIB chain of molecular weight in the range of about 200 to about 5000.
8. The composition on claim 1 wherein the PIBSA-derived surfactant has a
- 20 PIB chain of molecular weight in the range of about 300 to about 3000.
9. The composition on claim 1 wherein the alkylamine ethoxylate is selected from the groups comprising tallow amine penta ethoxylate, tallow amine tetra ethoxylate, tallow amine hexa ethoxylate, tallow amine hepta ethoxylate, oleyl amine deca ethoxylate, oleyl amine undeca ethoxylate,
- 25 oleyl amine nona ethoxylate, oleyl amine dodeca ethoxylate, tris(2-hydroxyethyl)-N-tallowalkyl-1,3-diaminopropane, oleyl amine penta ethoxylate, oleyl amine diethoxylate, stearyl alcohol penta ethoxylate, stearyl amine diethoxylate and combinations thereof.
10. The composition of claim 1 wherein the alkylamine ethoxylate is
- 30 selected from the groups comprising tallow amine penta ethoxylate, oleyl amine deca ethoxylate, tris(2-hydroxyethyl)-N-tallowalkyl-1,3-diaminopropane and combinations thereof.

11. The composition of claim 2 wherein the additive surfactant package is added to the following comprising:

- a) a hydrocarbon;
- b) a water;
- 5 c) optionally an antifreeze chemical; and
- d) optionally an ammonium nitrate.

12. The composition of claim 1 wherein surfactants are used in combination with the additive surfactant package but are not the additive surfactant package surfactants and include but are not limited to a) natural fats; b) 10 ionics excluding the additive surfactant package c) co-surfactants; d) fatty acids and their amine salts; e) ethoxylate alcohols and f) combinations thereof.

13. The composition of claim 2 wherein surfactants are used in combination with the additive surfactant package but are not the additive surfactant 15 package surfactants and include but are not limited to a) natural fats; b) ionics excluding the additive surfactant package c) co-surfactants; d) fatty acids and their amine salts; e) ethoxylate alcohols and f) combinations thereof.

14. The composition of claim 1 wherein the additive surfactant package is in 20 the range of about 0.01% to about 10% by weight of the water in oil composition.

15. The composition of claim 1 wherein the additive surfactant package is in the range of about 0.02% to about 5% by weight of the water in oil composition.

25 16. The composition of claim 2 wherein the PIB succinic acid - amine salt is prepared by reacting the PIB succinic acid with either an alkyl amine primary, secondary, or tertiary) or an ethanolamine and/or ethoxylated amine and wherein the salt can be a fully neutralised or partially neutralised salt.

30 17. The composition of claim 2 wherein a PIB succinic aminoalkylester or ester-acid or amine salt thereof is prepared by reacting the PIBSA or PIB succinic acid or ester thereof with a hydroxylamine or an alkanol amine like

ethanolamine and/or ethoxylated amine and, wherein the salt can be a fully neutralised or partially neutralised salt.

18. A process for making a water in oil emulsion comprising emulsifying a fuel, a water, a PIBSA-derived surfactant and an alkylamine ethoxylated surfactant to form an water in oil emulsion.

19. A process to produce an emulsified water in oil composition from a concentrate comprising emulsifying a portion of a fuel, a portion to substantially all of a water, substantially all of the PIBSA-derived surfactant, substantially all of an-alkylamine ethoxylated surfactant to form a concentrate emulsion; and then diluting the concentrated emulsion with the remaining portion of fuel and water at the time of use.

20. The process of claim 18 wherein an antifreeze chemical and an ammonium nitrate are added to the emulsification.

21. The process of claim 18 wherein the following components are added to the emulsification in combination with the additive surfactant package but are not the additive surfactant package surfactants and include but are not limited to a) natural fats; b) ionics excluding the additive surfactant package c) co-surfactants; d) fatty acids and their amine salts; e) ethoxylate alcohols and f) combinations thereof.

20

ABSTRACT

The invention relates to an emulsified water in oil composition using a novel additive surfactant package containing a PIBSA-derived surfactant with a molecular weight in the range of about 300 to 3000 and in the range of about 0.01% to about 10% by weight of the composition and an alkylamine ethoxylated surfactant in the range of about 0.01% to about 10% by weight of the composition.

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